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Towards Sustainable Production of Formic Acid from Biomass for Getting Hydrogen and Fuels

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Abstract

Formic acid is a widely used commodity chemical. It can be applied as a safe, easily handled and transported source of hydrogen or CO for different reactions including those producing fuels. The review includes historical aspects of formic acid production. It shortly analyzes the production based on traditional sources such as toxic CO, methanol and methane. However, the main emphasis is done to the sustainable production of formic acid from biomass and biomass-derived products via hydrolysis, wet and catalytic oxidation processes. New strategies of low temperature synthesis from biomass may lead to utilization of formic acid for production of fuel additives such as methanol, upgraded bio-oil, γ-valerolactone and its derivatives, as well as synthesis gas used for Fischer-Tropsch synthesis of hydrocarbons. Some technological aspects are considered.

Keywords: Formic acid; Production; Biomass; Hydrogen; Fuels

1. Introduction

Formic acid is a commodity that is widely used in the chemical, agricultural, textile, leather, pharmaceutical and rubber industries. Formic acid can substitute some inorganic acids in chemical processes and it is less corrosive than many of them. It also does not result in loading of nitrate, phosphate or sulfate into waste water.[1] According to the data of the European Chemical Agency, formic acid and the formate ion are readily biodegradable. Furthermore, formic acid and the formate ion are readily biodegradable in seawater.[2] The worldwide production capacity of formic acid was estimated to be up to 950 thousand tons per year.[3] European prices for 85% grade formic acid in the second quarter of 2014 were between €0.51-0.60/kg, while contract prices for June in the US were $0.60-0.70/kg.[4] The demand for formic acid is growing because of its relatively nontoxic and noncorrosive properties and this allows easy handling. It has been estimated that the market for this chemical will increase to 5.6% per year through 2019.[5]

Currently, formic acid is considered as one of the promising hydrogen storage materials due to a number of inherent advantages.[6] It is the simplest carboxylic acid and the products of its dehydrogenation are simple (H_2 and CO_2) and easily controlled (eq. 1):

$$HCOOH \rightarrow H_2 + CO_2. \quad (1)$$

In addition to the fact that hydrogen production from the decomposition of formic acid can be obtained under mild conditions, formic acid contains 4.4 wt% of hydrogen, approaching the Department of Energy (DOE) target of 5.5 wt% for efficient hydrogen storage materials. This value corresponds to high volumetric hydrogen content: 1 L of liquid formic acid contains 26.5 M of hydrogen (53 g H_2/L) whereas only 9.8 M of gaseous hydrogen can be stored in 1 L at the high pressure of 22 MPa.

Formic acid dehydration (eq. 2) may also take place in parallel to dehydrogenation, but, if the final goal is hydrogen, this reaction should be eliminated:

$HCOOH \rightarrow H_2O + CO.$ (2)

Alternatively, formic acid could be used for CO storage. In this case, the decomposition of formic acid (and its derivatives) to give CO can be performed over strong liquid acids[3, 7] and solid acid catalysts such as zeolites[8] or zirconia.[9]

It is also worth noting that formic acid can be utilized directly as a hydrogen donor instead of molecular hydrogen for hydrogenation (eq. 3) or deoxygenation (eq. 4) reactions:[10]

$RCH{=}CH_2 + HCOOH \rightarrow RCH_2CH_3 + CO_2,$ (3)

$RO + HCOOH \rightarrow R^1 + H_2O + CO_2.$ (4)

The latter reaction has potential for processes to convert biomass-related products containing high quantities of oxygen into valuable products, for example, into fuels. This application of formic acid provides the great advantage over molecular hydrogen that it is much easier and safer to store and transport formic acid. A requirement for this application is that formic acid would provide stable, CO-free hydrogen generation at low temperatures (about 373 K). This demand can be achieved by careful choice of a catalyst and reaction conditions and a significant amount of work on the decomposition of formic acid is currently in progress aimed at finding suitable combinations. At the same time, both the thermodynamic and kinetic aspects of the utilization of formic acid instead of molecular hydrogen should be taken into account before choosing formic acid as a hydrogen donor.

A promising new hydrogen storage technology, which consists of a reaction loop between carbon dioxide, hydrogen and formic acid/formates and mainly based on homogeneous catalysts has recently been reported (Figure 1).[11]

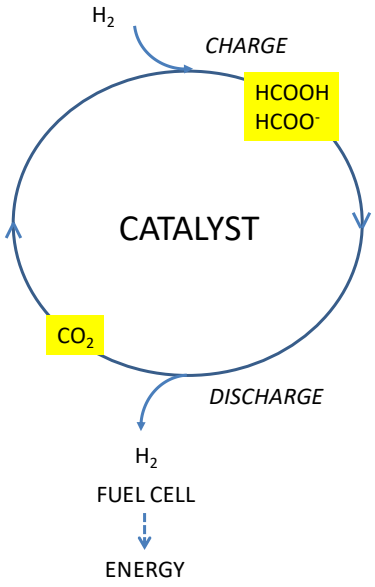

Figure 1. A catalytic loop for hydrogen storage.

Formic acid or formates are synthesized in this loop by reducing carbon dioxide with hydrogen at high pressures in the presence of bases or amines and this avoids the extra emission of this greenhouse gas. Hydrogen can be eliminated using a catalyst and be used for energy production in a fuel cell.

Recently, some reviews have appeared related to hydrogen production from formic acid mainly using homogeneous catalysis.[11b-d, 11h, 11j, 11k, 12] For example, Loges et al.[11h] in 2010 reported that the catalytic performance of some heterogeneous catalysts, including Pd/C, is far below that of homogeneous catalysts based on Ru complexes. This is also valid for some Ir complexes.[13] However, recently, important achievements have been reached in the field of heterogeneous catalysis using Pd-containing catalysts for gas-phase[14] and liquid phase[15] dehydrogenation of formic acid. Heterogeneous catalysts possess the important advantages of easy handling and separation. This recent interest in hydrogen production from formic acid has been paralleled by the development of methods for the production of formic acid from CO_2 and renewable biomass.

In this review, we will shortly consider historical aspects of formic acid production as some of them are related with modern formic acid production and especially with production of formic acid from biomass feedstocks. We will have a look on the production of formic acid from CO, methanol and methane. Then, we will discuss recent advances in the area of formic acid synthesis from biomass and biomass-derived products by hydrolysis, wet oxidation and catalytic oxidation. Finally, we will finish with utilization of formic acid for production of fuels as it was not discussed almost earlier. In the present review we will not consider production of formic acid or formates by hydrogenation of CO_2, as it is thoroughly reviewed very recently for homogeneous catalysts,[12-13] but, probably, still demands a further consideration for the heterogeneous catalysts despite some discussion is already present in the literature.[16] We will not also discuss enzymatic, microbial, electrochemical or photochemical production of formic acid and formates.

2. Historical aspects of formic acid production

Historically, formic acid production commenced with biomass-based precursors. Careful analysis of old methods has already given new ideas for the production processes and it is to be hoped that this approach can still give new developments. Hence, we first consider approaches based on historical methods. Figure 2 shows developments for the formic acid synthesis.

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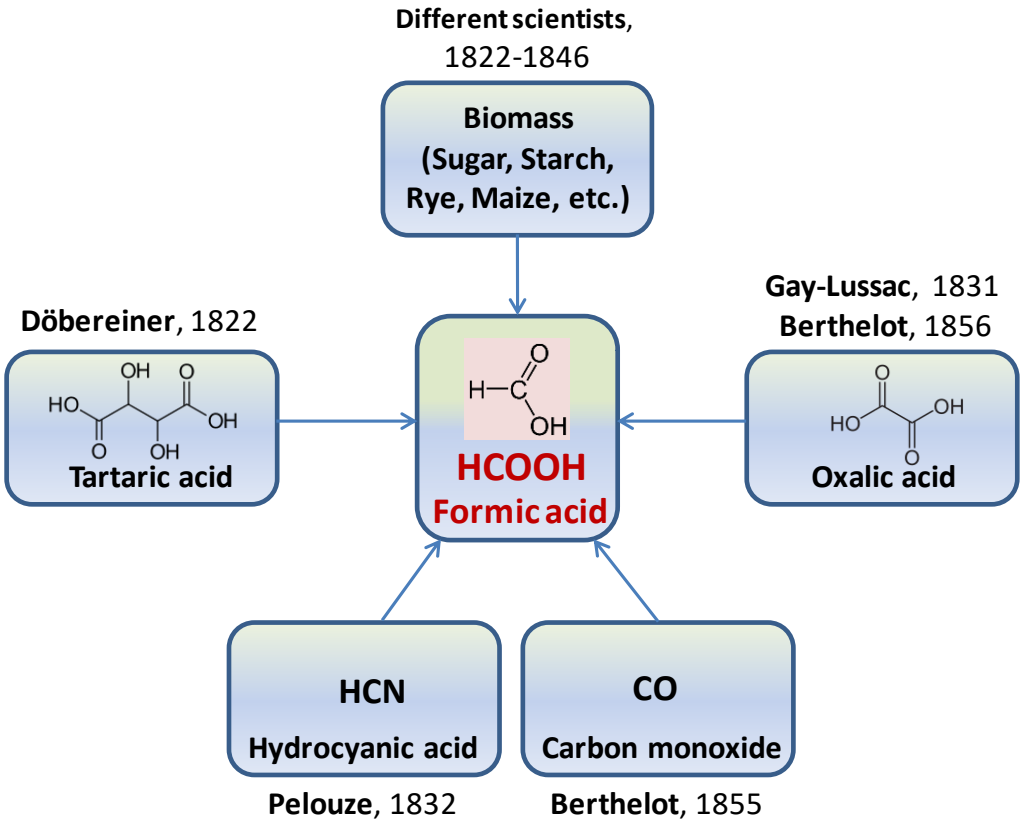


Figure 2. Historical developments for the formic acid synthesis.

In 1822, the German chemist Döbereiner performed a synthesis of formic acid from the tartaric acid that occurs in plants (mainly in grapes) using dilute sulfuric acid with the addition of manganese oxide (black), probably, used as a catalyst.[17] Earlier, formic acid was synthesized by distillation of ants.[18] At the same time, Döbereiner also reported that by heating anhydrous sulfuric acid brings about formic acid decomposition to give CO and water (eq. 2).[7, 17b] Interestingly, he used this reaction to determine the composition of formic acid. Other chemists including Gmelin[19] and Liebig[19b] showed that different biomass-derived feedstocks like plant roots, ligneous materials, sugar, starch, etc. could be used as starting materials instead of tartaric acid. The American chemist J.P. Emmet,[20] while carrying out a similar synthesis using rye and maize as starting materials, showed in 1837 that the manganese oxide is not necessary for the reaction and that this compound can even bring about (catalyze) the decomposition of formic acid. Hence, this synthesis approach can be considered mainly as a hydrolysis.

The yield of formic acid produced from sugar was insignificant, as the formic acid was mixed with other products. Hence, another process was suggested by two brothers William Barton Rogers and Robert Empie Rogers, in 1846; in their approach, sugar was added to a solution of potassium dichromate and distilled with the slow addition of sulfuric acid, this giving a nine-fold increase in yield.[21]

In 1831, the French chemist Gay-Lussac performed the thermal decomposition of oxalic acid in the presence of sulfuric acid and found some quantities of formic acid among the products.[22] Oxalic acid was earlier synthesized from sugar by reaction with concentrated nitric acid. However, we have not found any evidence that Gay-Lussac synthesized formic acid from hydrocyanic acid as is sometimes mentioned in the literature.[18c] This was done in 1832 by the French chemist Pelouze[23] who was a laboratory assistant to Gay-Lussac from 1827 to 1829. His synthesis involved interaction of hydrocyanic acid with fuming hydrochloric acid, which contains water.

Later, in 1855, the French chemist Berthelot reported the synthesis of potassium formate from CO and wet caustic potash (KOH) at 373 K (eq. 5):[24]

$$KOH + CO \rightarrow KHCOO, \qquad (5)$$

He then treated the product with sulfuric acid (eq. 6) and performed distillation to get formic acid:

$$KHCOO + H_2SO_4 \rightarrow HCOOH + KHSO_4. \qquad (6)$$

Acidolysis of alkali formates is still used in industrial production of formic acid contributing by about 20% to the total production.[3] In 1856, Berthelot also synthesized formic acid by a reaction of oxalic acid and glycerol at 373 K for 12-15 h.[25] In this process, monoformate of glycerol was formed as an intermediate product, which, upon distillation with water, decomposed into glycerol and formic acid.

It is worth noting that the first account of the dehydrogenation of formic acid vapor (eq. 1) using a heterogeneous catalyst (Pt black) was by Berthelot[17a, 26] in 1864, and not by the Nobel laureate Sabatier working with Mailhe[27] as is often assumed,[11h, 28]; the report of their studies of this reaction was published almost 50 years later.

Formates can be obtained by hydrogenation of carbonates and bicarbonates by hydrogen at high pressure using metal catalysts (eq. 7, where M is an alkali metal):

$MHCO_3 + H_2 \rightarrow MHCOO + H_2O.$ (7)

This reaction was first carried out in 1914 by Bredig and Carter who used Pd black as catalyst.[29] Hence, many approaches to synthesize formic acid and formates were proposed during the 19th century and beginning of the 20th century.

3. Formic acid production based on fossil feedstocks

Figure 3 shows the basic reactions which will be considered in this section. We will review first the traditional industrial method of formic acid production and then discuss some novel approaches. By fossil feedstocks we mean natural gas (methane) or coal, which could be used for the synthesis of CO precursor.

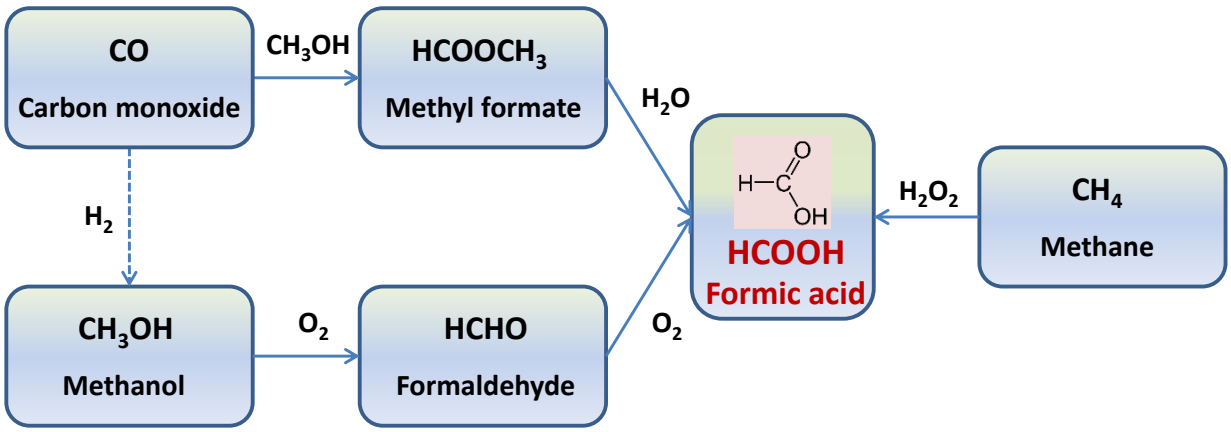


Figure 3. Formic acid production based on CO, methanol and methane.

Formic acid from CO. Hietala et al.[3] have discussed excellently the presently used BASF technology for the formic acid production. In the first step of this process, CO reacts with methanol in the presence of a strong base (Na methoxide) to produce methyl formate. This step is performed at high pressure (4 MPa), but at relatively low temperatures of about 353 K (eq. 8), with a selectivity of 96%. In the second step, hydrolysis of methylformate is performed to produce formic acid and methanol (eq. 9):

$$CO + CH_3OH \rightarrow HCOOCH_3, \quad (8)$$

$$HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH. \quad (9)$$

The sum of these reactions gives the reaction:

$$CO + H_2O \rightarrow HCOOH, \quad (10)$$

implying that the consumed reactants for the formic acid synthesis are CO and water. The flow-sheet of the process is presented in Figure S1.

A 100,000 t/a formic acid plant began operating in Ludwigshafen (Germany) in 1981. In this plant, a new technology for the hydrolysis and dehydration was used for the first time. A technology of methylformate production from methanol has a much longer history. Up to 80% of the present synthesis of formic acid is performed via hydrolysis of methyl formate.[3]

An advantage of the BASF process is that it is well established process with a long history implying high reliability. It allows obtaining formic acid in high concentration (up to 98%). At these concentrations formic acid is substantially less corrosive than in diluted solutions.[3] Recyclability of some intermediates like methanol, main part of water and secondary amide, used for extraction of formic acid, is a very important feature of the process. The process has, of course, some drawbacks. For example, the alkali methoxide catalysts are corrosive and harmful base catalysts. They are very sensitive to moisture and CO_2. Interaction with these impurities may cause operational problems, for example, plugging owing to the formation of sodium formate or carbonate. The process consists of complicated multisteps, which consume a large amount of energy. Many separation steps are needed to separate formic acid from intermediates resulting in high costs. Finally, it uses toxic carbon monoxide which is normally produced in unsustainable way from coal or natural gas at very high temperatures (>900 K). Moreover, methylformate is decomposed in a high excess of water (5:1) to shift the equilibrium to formic acid and methanol. However, recently an improvement based on using a tertiary amine has been proposed by BASF allowing to decrease the amount of water necessary for hydrolysis of methylformate.[30] Hence, other approaches of formic acid synthesis could be considered.

Formic acid from methanol by oxidation. A novel less costly technology has recently been developed in the Boreskov Institute of Catalysis (Figure S2).[31] Using this technology, methanol oxidation to give formaldehyde (eq. 11) using an iron-molybdenum catalyst is carried out at the first step with a yield of 90-92% at 540-673 K; the formaldehyde obtained is then oxidized to give formic acid (eq. 12) using tubular reactors containing an appropriate vanadia-titania catalyst to give a yield of 87-88% relative to the converted formaldehyde in the second step at low temperatures (373-403 K):

$$2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O, \qquad (11)$$

$$2HCHO + O_2 \rightarrow 2HCOOH. \qquad (12)$$

A pilot plant with a capacity of 2–3 kg of formic acid per hour has been constructed and tested. In this plant, methanol with a flow rate of 2.5–3.0 kg per hour was pumped into a vaporizer and mixed with preheated air with a flow rate of 25–30 Nm^3/h, thus creating a composition of 6.5 vol % of formaldehyde in air. Hence, the used initial methanol concentration was close to the lower explosion limit. A concentration of formic acid in the condensate was 58–62 wt% providing the yield of 79-81% relative to the converted methanol. As was mentioned, to obtain formic acid of commercial quality this condensate should be subjected to one-stage distillation.[31a]

Danilevich et al.[32] showed that the activity of vanadia/titania catalysts in the oxidation of formaldehyde to formic acid is associated with the presence of monolayer vanadia species while bulk vanadium oxide was less active. A similar conclusion applied to the oxidation of some hydrocarbon molecules and oxygenates on this type of catalyst.[33]

Currently, 40% of the methanol produced worldwide is used for the production of formaldehyde by eq. 11.[34] Hence, a second reactor for the oxidation of formaldehyde according to eq. 12 could be even attached to existing facilities.

Formic acid from methane by oxidation. CO and hydrogen production from fossil feedstocks demands very high temperatures (>900 K) being unsustainable. Methanol is normally produced from CO and H_2. The advantage of utilization of methane as a source of carbon for formic acid production is that it is nontoxic and present on our planet in high amounts providing low price. However, the drawbacks are its high flammability and remoteness of the reserves demanding relatively expensive transportation. Inertness of methane also limits its utilization as a carbon source and is explained by the presence of very strong C-H bonds. However, attempts to convert methane to valuable products using heterogeneous catalysts have been widely performed.[35] These efforts included work on the catalytic oxidation of methane to methanol. However, formic acid is often obtained as a main product instead of methanol in these studies. All works have been performed with hydrogen peroxide as a source of oxygen.

Wei et al.[36], used a vanadium based compound ($VOSO_4$) to produce formic acid from methane at 333 K; however, the yield was low (<5%). ZSM-5 zeolite catalysts containing Fe have been a subject of broader studies. Thus, Rahman et al.[37] reported the production of formic acid with a yield of 13% and a selectivity of 67% using a ZSM-5 zeolite at 2.6 MPa and 373 K. Hutchings et al.[38] showed recently that methane can be oxidized over a Fe-ZSM-5 catalyst at 323 K giving formic acid as the main product. The reaction proceeded with methyl hydroperoxide as the primary product; this then reacted to form methanol which was sequentially oxidized to formic acid and finally to CO_2. As a result of EXAFS and DFT studies, the authors assigned the activity to the presence of a di-iron complex containing two octahedral Fe^{3+} sites: $[Fe_2(\mu_2\text{-}OH)_2(OH)_2(H_2O)_2]^{2+}$. This intermediate can then be activated by H_2O_2 to produce a (Fe^{4+}=O) site capable of oxidizing methane to give the methyl hydroperoxide intermediate and water in a closed catalytic cycle.

It is possible that the catalytic activity of the ZSM-5 zeolite in the paper of Rahman et al.[37] should be also assigned to the same Fe sites. At least these authors indicated that their zeolites contained iron (0.02-0.11 at%). Boltenkov et al.[39] recently reported a selectivity of 84% for the production of formic acid at the conversion of methane of 1% in experiments using the same type of zeolites and conditions close to those used by the Hutchings group.

The advantage of the oxidation of methane using these approaches is the low temperature. Hence, these studies show promise, but now the technical feasibility of this process looks low. Also, hydrogen peroxide is a relatively expensive oxidizing agent. Despite of these notes a process for formic acid production from methane can be developed basing on the process of methanol production by methane oxidation patented by UOP in 2007 (Figure S3)[40] if the development of catalysts for the former reaction will be progressed further.

4. Formic acid production from biomass-derived feedstocks by hydrolysis

Formic acid has been produced directly with relatively high yields from biomass and from all its components: hemicellulose, cellulose, lignin and vegetable oils, using hydrolysis and oxidation. Evidently, some activation/pretreatment of biomass has to be performed for efficient processing.[41]

Formic acid from hemicellulose. Xing et al.[42] reported a process giving furfural, formic and acetic acids using a continuous two-zone biphasic reactor. In the first zone, formic and acetic acids were obtained by acid hydrolysis of aqueous hemicellulose solutions, i.e. the depolymerization of xylose oligomers into xylose monomers and the hydrolysis of formylated and acetylated xylose oligomers into formic acid and acetic acid, respectively. The second zone was designed to dehydrate xylose monomers into furfural, this being the main product. The authors reported that on the basis of this approach a plant can be built that could have a capacity of 78 kiloton per year of furfural, 12 kiloton per year of formic acid and 44 kiloton per year of acetic acid (processing 160 ton per hour of hemicellulose solutions with a xylose concentration of 10.7 wt%). Using this process, the authors aimed for a significant decrease of the selling price of furfural by attaining an output of 25% of that required by the U.S. market.

Formic acid from cellulose by pyrolysis. A significant yield of formic acid, up to 40 wt%, could be obtained by fast pyrolysis of cellulose at 923 K.[43] However, this approach demands high temperatures and gives a range of additional products, this implying nonselective formic acid production. Hence, conversion of cellulose to formic acid by hydrolysis and oxidation is preferable.

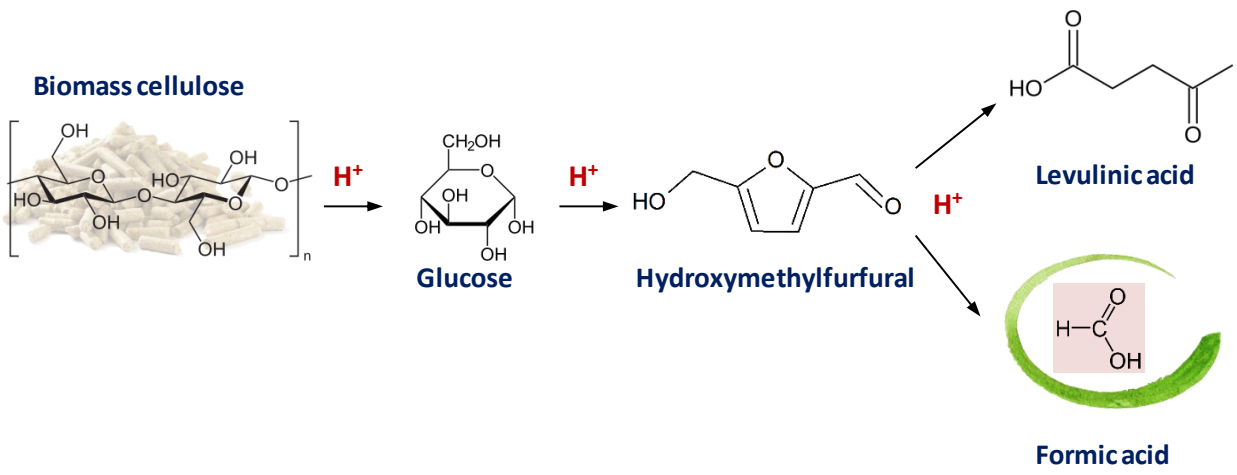


Figure 4. Formic acid production from cellulose by hydrolysis.

Formic acid from cellulose by hydrolysis with acids. Formic acid is produced in high concentration as a by-product in the production of levulinic acid from cellulose (Figure 4). Hydroxymethylfurfural is an intermediate of this reaction and both the levulinic acid and hydroxymethylfurfural are important platform molecules.[44] In this reaction, cellulose is first converted through hydrolysis to produce glucose. The glucose then yields hydroxymethylfurfural by several dehydration steps through loss of three water molecules. A rehydration step involving the addition of two water molecules is then needed to get almost equimolar quantities of levulinic acid and formic acid.[45] The acid-catalyzed conversion of carbohydrates into levulinic acid and formic acid, as well as of cellulose into glucose, can be carried out in concentrated solutions of acids at moderate temperature (≈373 K) or in their dilute solutions at elevated temperature (>433 K).[46] As was mentioned above, formic acid decomposes already at about room temperature in, for example, concentrated sulfuric acid[7] and this can decrease the acid yield.

Recently, the Biofine process, based on a two-step hydrolysis of lignocellulosic biomass using diluted sulfuric acid, was developed and applied for the conversion of various biomass feedstocks, including agricultural residues, paper sludges and the organic fraction of municipal waste.[47] Lignin is converted to char. Any hemicellulose present in this process is converted into

furfural ($C_5H_4O_2$). It should be noted that formic acid could be also obtained as a result of hydrolytic fission of the aldehyde group in the furfural.[42, 48]

Formic acid from cellulose by hydrolysis with solid acid catalysts. It has been shown that the use of solid-acid catalysts for the hydrolysis process produces lower amounts of wastes and allows easier separation of these wastes from the products than when using liquid acids. Joshi et al.[49] reported good yields of levulinic acid and formic acid from a one-pot hydrothermal conversion of cellulose in water using a zirconium dioxide as a catalyst at 453 K. The yield of formic acid was however higher when using a ZSM-5 zeolite and reached 45%. Ahlkvist et al.[50] used a macroporous acidic ion-exchange resin, Amberlyst-70, as a catalyst and obtained the maximum theoretical yields of 59 and 68 mol% for formic and levulinic acids, respectively, in a one-pot synthesis at 453-473 K. At present, formic acid is considered only to be a by-product of such a hydrolysis process, requiring a use, while the main product is levulinic acid.

5. Formic acid production from biomass-derived feedstocks by wet oxidation

Formic acid production processes from biomass-derived feedstocks by oxidation can be arbitrarily separated into those which use redox catalysts and those which do not use redox catalysts. The latter production has been carried out by wet oxidation, i.e. oxidation at high pressures of oxygen (1-5 MPa) in the presence of water at temperatures 423-503 K. It is often performed in the presence of acids or alkalis, which could affect the reaction as acid-base catalysts. The wet oxidation of organic compounds normally proceeds via a free radical

Table 1. Some catalysts and their catalytic properties in the production of formic acid from biomass and biomass derived products by wet and catalytic oxidation.

Biomass product	Catalyst	Solvent	Temperature/ K	Oxidant (pressure/MPa)	Formic acid yield, %	Reference
Wood	-	H_2O	463	O_2 (3.3)	20	McGinnis et al. [51]
Bio-oil	H_2SO_4	H_2O	443	O_2 (5)	56	Müller et al.[52]
Lignin	NaOH	H_2O	473	O_2 (1)	44	Demesa et al.[53]
Glucose	NaOH	H_2O	523	H_2O_2, O_2	75	Jin et al.[54]
Saccharides	NaOH	H_2O	423	H_2O_2, O_2 (3.1)	85	Yun et al.[55]
Cellulose	$NaVO_3$, H_2SO_4	H_2O	433	O_2 (3)	65	Wang et al.[56]
Cellulose	Sulfonated Fe(III) porphyrin, NaOH	H_2O	423	O_2 (2)	64	Liu et al.[57]
Cellulose	$H_4PVMo_{11}O_4$	H_2O	453	O_2 (0.6)	68	Zhang et al.[58]
Cellulose	$Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$, H_2SO_4	H_2O	433	O_2 (2)	66	Gromov et al.[59]
Cellulose	$H_5PV_2Mo_{10}O_{40}$	H_2O, Toluenesulfonic acid	363	O_2 (3)	31	Wasserscheid et al.[60]
Hemicellulose	$H_5PV_2Mo_{10}O_{40}$	H_2O, Toluenesulfonic acid	363	O_2 (3)	58	Wasserscheid et al.[60]
Lignin	$H_5PV_2Mo_{10}O_{40}$	H_2O, Toluenesulfonic acid	363	O_2 (3)	32	Wasserscheid et al.[60]
Beech wood	$H_5PV_2Mo_{10}O_{40}$	H_2O, Toluenesulfonic acid	363	O_2 (3)	61	Wasserscheid et al.[60]
Blue-green algae	$H_5PV_2Mo_{10}O_{40}$	H_2O, Toluenesulfonic acid	363	O_2 (3)	40	Albert and Wasserscheid[61]
Glycerol	$H_6PV_3Mo_9O_{40}$	H_2O	423	O_2 (2)	60	Zhang et al.[62]
Glycerol	$Ru(OH)_4$/reduced graphite oxide +$FeCl_3$	H_2O	433	O_2 (0.5)	60	Xu et al.[63]
Glycerol	Fe(III) salts	H_2O	room	H_2O_2	94-99	Farnetti and Crotti[64]

mechanism.[65] Some examples of the oxidative conversion of biomass feedstocks into formic acid without redox catalysts are shown in Figure 5 and Table 1.

Formic acid from wood biomass. In 1983, McGinnis et al.[51] converted three types of wood biomass into a mixture of formic acid, acetic acid, methanol and other acids by wet oxidation; gaseous and solid products were also formed. Formic acid was the main product, obtained with a yield of 20% without a catalyst at 3.3 MPa of oxygen and 463 K. The concurrent yield of acetic acid was a factor of 2-3 lower. Addition of 0.67% $FeSO_4$ as a catalyst led to an increase of the formic acid yield.

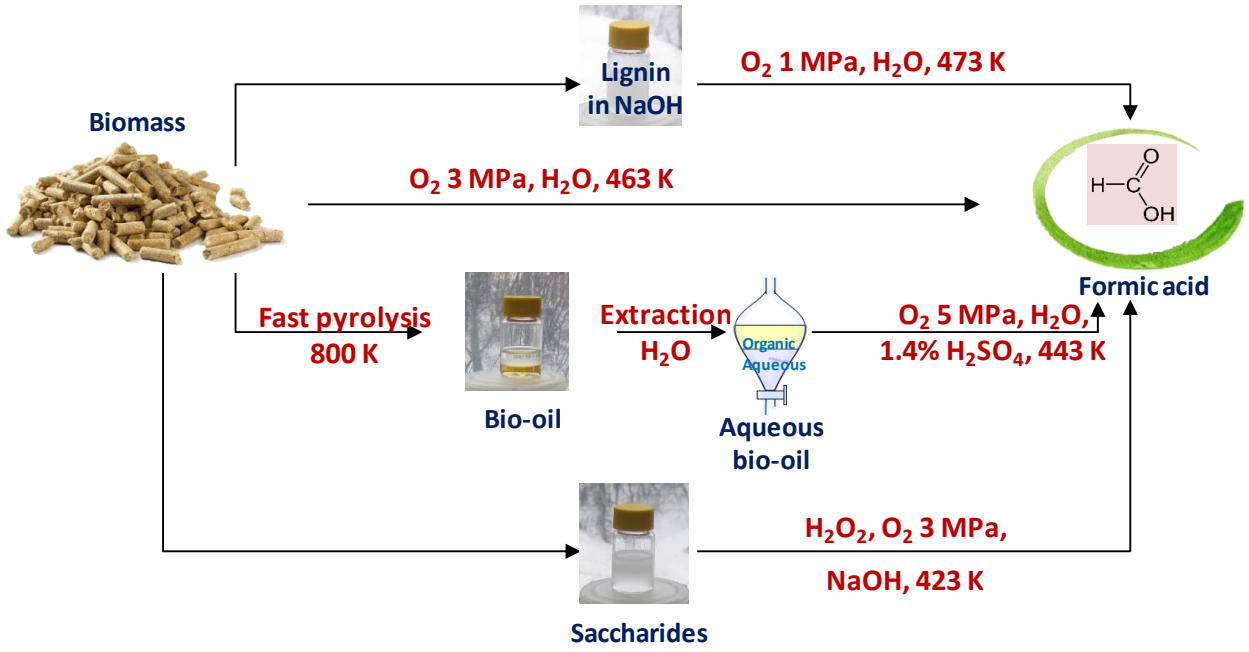


Figure 5. Formic acid production by wet oxidation of biomass and biomass-derived products.

Formic acid from bio-oil. Bio-oil obtained by fast pyrolysis of biomass is a viscous mixture of hydrocarbons, oxygenates and water and it contains a significant amount of oxygen.[10a] To obtain fuels and fuel additives from this mixture it must be upgraded. The upgrading process involves a decrease of the content of oxygen and water as well as a decrease of the viscosity of the bio-oil.

Müller et al.[52] performed fast pyrolysis of *Pinus radiata* sawdust at 800 K followed by extraction of the aqueous bio-oil phase with water and wet oxidation of the product obtained. They added sulfuric acid as a catalyst (1.4 wt%) to enhance the hydrolysis of some oxygenates. The authors also performed an intermediate extraction of the aqueous phase of the bio-oil with butyl acetate to remove low-molecular-weight phenolic compounds. These phenolic compounds are formed as a result of the conversion of lignin and are known to act as inhibitors in the noncatalytic oxidation of organic compounds providing annihilation of radicals.[65] Formic acid was the main product of the reaction and was obtained with a yield up to 56 wt%. The authors also noted that the content of solid and gaseous products in their process was low. They proposed that the formic acid could be used further as a hydrogen source for upgrading the remaining organic phase of the bio-oil.

Formic acid from lignin. Demesa et al.[53] reported that alkali lignin could be converted to a mixture of acids by wet oxidation at 0.5-1.5 MPa of oxygen in basic medium and temperatures in the range 443 - 498 K. Formic, acetic and succinic ($C_4H_6O_4$) acids were the main products obtained, all in approximately the same concentrations. At a low concentration of lignin (4 g/L), the yield of acids was higher (44%) than that (16%) when a high concentration of lignin was used (40 g/L). The authors indicated that the undesirable decomposition of formic acid started at temperatures higher than 473 K.

Formic acid from glucose and other saccharides. It is easier to convert glucose and other carbohydrates into formic acid and formate salts than it is to convert cellulose. For example, Jin et al.[54] have reported that transformation of glucose into formate salts with an excellent yield of 75% is possible in the presence of alkali by hydrothermal oxidation with excess of H_2O_2 using a batch reactor at a mild temperature of 523 K. In fact, at these conditions hydrogen peroxide converts to oxygen and water. In the absence of alkali, the yield of formic acid was only about 24%.

Jin et al.[54] indicated that the oxidation of hexose (glucose) takes place first via the –CHO group forming gluconic acid. The formation of six molecules of formic acid from one molecule of glucose (eq. 13):

$$C_6H_{12}O_6 + 6H_2O_2 \rightarrow 6HCOOH + 6H_2O \qquad (13)$$

is possible if the mechanism of the conversion of gluconic acid involves α-position (C1-C2) scission in the molecule. However, if the mechanism involves β-position (C2-C3) scission, the formation of oxalic acid takes place. The further reactions of oxalic acid may occur not only in the direction of the formic acid production, but also in the direction of the formation of CO_2, which decreases the yield.

Yun et al.[55] have recently reported the use of NaOH for wet oxidation to convert mono- and disaccharides to formic acid with a yield of 85% at 423 K. The alkali was found to have two roles in enhancing the production of formic acid. One was inhibition of the formic acid decomposition and the other favored the selective oxidation at the C1 position of the hexoses, leading to the formation of formic acid via the rupture of the C1–C2 bond. Similar mechanism could work probably for synthesis of formic acid from hemicellulose.

6. Formic acid production from biomass-derived feedstocks by catalytic oxidation

As is seen in the previous section catalysts normally give improvement for the different processes of formic acid production from biomass-derived products. In this section we will consider the effect of redox catalysts. Some examples are shown in Table 1.

Formic acid from cellulose with vanadate and Fe containing catalysts. Formic acid can also be obtained by a combination of acidic hydrolysis and catalytic oxidation of cellulose. We will consider only the most important relevant publications reporting high yields of formic acid. Generally, the oxidation of cellulose involves two steps, which proceed on different sites: transformation of cellulose to glucose on acidic sites and partial oxidation of the glucose obtained to formic acid on redox sites (Figure 6).

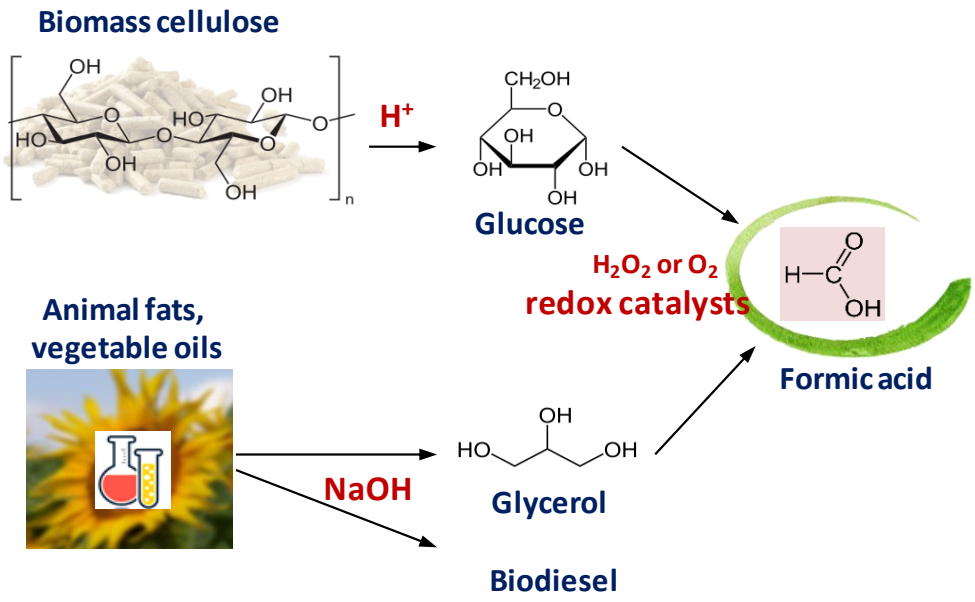


Figure 6. Formic acid production by catalytic oxidation of biomass-derived products.

To perform a one-pot process, either a mixture of an acidic catalyst with a redox catalyst or a single catalyst with bifunctional properties combining acidic and redox properties is needed. One molecule of glucose is expected to give 6 molecules of formic acid (eq. 14):[65]

$$C_6H_{12}O_6 + 3O_2 \rightarrow 6HCOOH. \qquad (14)$$

Wang et al.[56] showed that the conversion of cellulose or hemicelluloses to formic acid can be achieved in the presence of sodium metavanadate, sulfuric acid and oxygen at 433 K, and reported yields of about 65%. The system efficiency can be assigned to the high performance of VO_2^+ species combined with the acidity provided by sulfuric acid (0.7 wt%) leading to hydrolysis

of the cellulose in the first step. The same group of authors[66] for the same catalyst proposed a mechanism of the formation of products including formic acid in the combined hydrolysis/oxidation process (Figure 7). It is seen that the conversion of cellulose into formic acid is complex and includes several simultaneous and/or successive reactions. These reactions affect each other, and thus affect the whole conversion process and product distribution. The authors managed to separate two hydrolysis and two oxidation steps occurring during the conversion. It is seen from the scheme that formic acid can be obtained by oxidation of glucose, hydroxymethylfurfural and furfural.

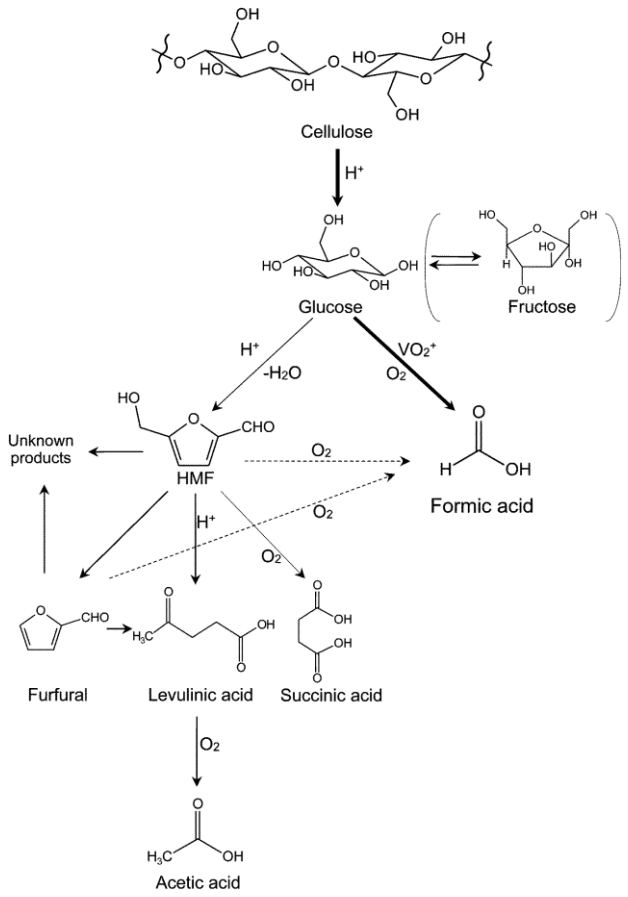


Figure 7. A scheme for the formation of products from cellulose in a combined hydrolysis/oxidation process with $NaVO_3$-H_2SO_4 as a catalyst and oxygen as oxidant. Reproduced from Ref.[66] with permission from The Royal Society of Chemistry.

Alkalis can also be used instead of acids for the first step of cellulose conversion, hydrolysis. Liu et al.[57] used a bio-inspired conversion of cellulose using sulfonated Fe(III) porphyrin as the catalyst in an aqueous NaOH solution using O_2 (2 MPa) as the oxidant and obtained a yield of 64% for formic acid at 423 K.

Formic acid from cellulose with heteropoly acids as catalysts. Heteropoly acids combine both acidic and redox properties. These can be tuned by varying their chemical composition.[67] The group of Wasserscheid[68] has demonstrated that water-soluble carbohydrates could be fully and selectively converted to formic acid and CO_2 at temperatures 373 K and lower using an oxygen pressure of 3 MPa over a Keggin-type $H_5PV_2Mo_{10}O_{40}$ polyoxometalate. In similar studies, Li et al. [69] showed that cellulose could be converted to give a yield of 35% of formic acid at a higher temperature (443 K) using a catalyst with the same composition. Zhang et al.[58] reported that formic acid could be obtained with a higher yield of 68% by the oxidation of cellulose by oxygen at a relatively low pressure of 0.6 MPa using a phosphovanadomolybdic acid ($H_4PVMo_{11}O_{40}$) catalyst at 453 K. Acetic acid was obtained as a by-product. Gromov et al.[59] obtained formic acid with a yield of 66% from a mechanically-activated microcrystalline cellulose using a Co-Mo-V-P heteropoly acid at 433 K. They also observed a linear dependence of the reaction rate on the concentration of protons in the solution for different heteropolyacids, this indicating that the hydrolysis of cellulose to glucose (Figure 6) limits the rate of the reaction. They found that the apparent activation energy of the process was 78 kJ mol^{-1}, this value being much lower compared to the apparent activation energies found for the processes of cellulose hydrolysis using a solution of sulfuric acid as a catalyst (170–180 kJ mol^{-1}).

Recently, the group of Wasserscheid[70] reported even better results than in their earlier paper[68] and demonstrated that formic acid yields of up to 85% could be obtained from glucose at temperatures as low as 363 K using 2 MPa of oxygen. This result was realized by applying another polyoxometalate, $H_8PV_5Mo_7O_{40}$, as a homogeneous catalyst, oxygen as an oxidant and water as a

solvent in the presence of a long-chain primary alcohol as an in-situ extracting agent. They noted that there is no reason to use harsher conditions for oxidation, as temperatures higher than 363 K and strongly acidic solutions may decrease the yields of formic acid because of the conversion of substrates to other products and of formic acid to CO and water.

Formic acid from other biomass sources. Reaching a significant progress in conversion of first generation biomass (sugars, starch, vegetable oils) to formic acid using polyoxometalates as catalysts, Wasserscheid et al.[71] have also converted water-insoluble biomass feedstocks using $H_5PV_2Mo_{10}O_{40}$ as the homogeneous catalyst, oxygen as the oxidant (3 MPa), water as the solvent and p-toluenesulfonic acid as a solubility and depolymerization promoter. They managed to convert wood, waste paper, xylan or even cyanobacteria (blue-green algae) to formic acid and CO_2. With added p-toluenesulfonic acid, the 66 h experiments resulted in 100% combined formic acid + CO_2 yield for xylan and lignin. At these conditions a 68% combined formic acid + CO_2 yield was obtained for cellulose. Cyanobacteria as a third generation of biomass was converted with a 71% combined yield and 56% selectivity to formic acid. Later, the group proved high yields for conversion of other kinds of third generation biomass like red and green algae.[61]

The group has set up the OxFA Company to continue the development of the process; up scaling has been performed and a continuously operating plant has been built. The authors showed that yields of formic acid in their OxFA plant from cellulose, hemicelluloses, lignin and beech wood using a polyoxometalate catalyst consist of 31, 58, 32 and 61%, respectively.[60] Generally, it was concluded that any biomass could be converted to formic acid with high yields using polyoxometalates as catalysts at 363 K. That is a very important result allowing thinking, how formic acid produced from biomass could be used further, for example, for providing hydrogen and carbon for synthesis of fuels and other chemicals.

Formic acid from glycerol. As the production of biodiesel by the transesterification of vegetable oil and animal fats is steadily increasing and had already reached 2.9 billion gallons per

year in the U.S. in 2016,[72] the question of the utilization of the glycerol obtained as a by-product in the process has become very important. At the present time, the prices of glycerol and formic acid are comparable (approximately US$ 0.3 per pound); however, the price of glycerol is decreasing significantly because of an increase of biodiesel production.[62] Thus, the synthesis of formic acid from glycerol could become important. A number of the papers devoted to this subject will now be summarized.

An energy efficient process has been proposed by Zhang et al.[62] for the selective oxidation of glycerol over vanadium substituted phosphomolybdic catalysts in aqueous solution. The selectivity to formic acid reached 60% at full conversion of glycerol in a 1 wt% solution using an $H_6PV_3Mo_9O_{40}$ catalyst at 2 MPa of oxygen and at a temperature of 423 K. Ntho et al.[73] used heterogeneous Au catalysts supported on Al_2O_3 in the oxidation of glycerol at 0.9 MPa of oxygen at 363 K and showed that, if the Au particles were relatively large (20 nm), formic acid was a main product of oxidation at high conversion. Xu et al.[63] demonstrated that large quantities of formic acid could be obtained from the oxidation of glycerol with molecular oxygen over $Ru(OH)_4$ nanoparticles (1.3 nm) supported on reduced graphite oxide in the presence of $FeCl_3$; the yield of formic acid was 60% at 433 K. Farnetti and Crotti[64] showed that oxidation of glycerol could be performed effectively using iron salts and hydrogen peroxide, giving yields of 94-99%; in this case, the oxidation took place even at room temperature in water. It is likely that there will be much work on this topic as a consequence of further decreases of glycerol price.

7. Formic acid for production of fuels and fuel additives

Formic acid can be used for the production of various fuels and fuel intermediates, examples being γ-valerolactone ($C_5H_8O_2$) and methanol, as well as the production of synthesis gas used for the

Fischer-Tropsch synthesis (Figure 8). It can be also used as a hydrogen source for upgrading of bio-oil obtained by fast pyrolysis from biomass.

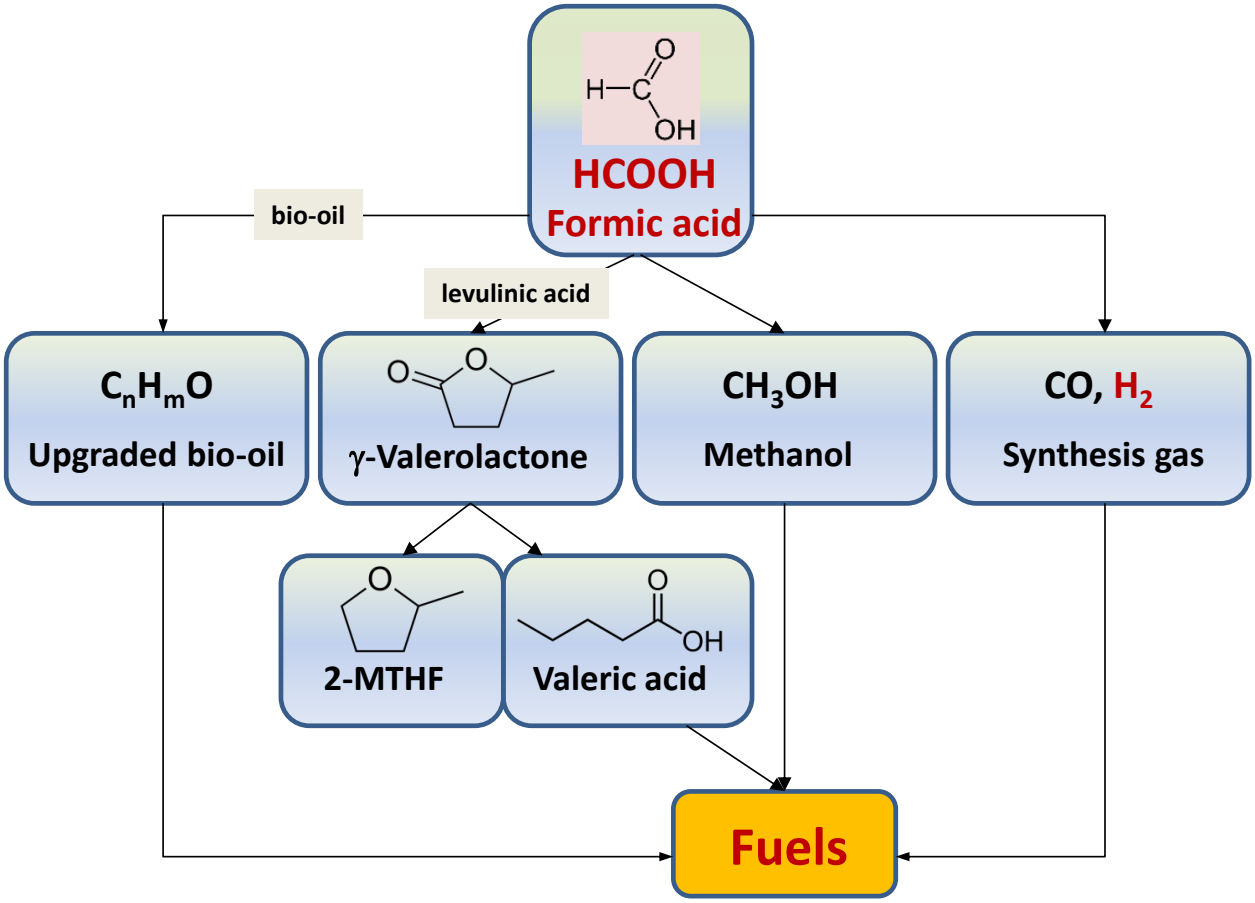


Figure 8. Possible production of fuels using formic acid.

Conversion of bio-oil to hydrocarbons with formic acid. Elliot[74] has reported that performing bio-oil upgrading in the presence of hydrogen donor molecules leads to improvement of the bio-oil quality and it was found that less deactivation of the catalyst occurred in this case. We have proposed using of formic acid and catalysts for upgrading of bio-oil to fuel additives.[10a] This upgrading could take place according the following reaction (eq. 15):

Bio-oil + HCOOH → Upgraded Bio-oil + (H_2O) + CO_2. (15)

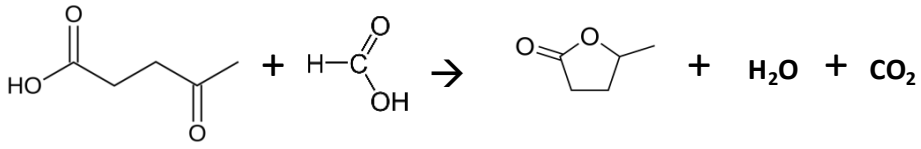
Recent experimental studies confirmed that upgrading of bio-oil and model compounds using formic acid as a hydrogen source are really promising.[75] Thus, Tan et al.[75c] hydrogenated the

model compounds, furfural and phenol, using Pd/C and Ni catalysts at 573 K. The main product of furfural hydrogenation was furfuralcohol, while the phenol was hydrogenated to give mainly cyclohexanone and cyclohexanol. The furfuralcohol could be used as a rocket fuel. Phenols are known poisons for different catalysts used for bio-oil upgrading. Hence, a decrease of their content in bio-oil may provide an increase in the stability of the bio-oil upgrading catalysts.

Xu et al.[75b] used Ni supported on mesoporous carbon to hydrogenate a model bio-oil compound and a raw bio-oil with formic acid, methanol or ethanol as hydrogen donors at 500 K. Formic acid effectively converted ethylene glycol, o-cresol and acetone in the model bio-oil compound as compared to other hydrogen donors. Using the raw bio-oil, the authors showed that the content of phenolic compounds decreased after hydrogenation with formic acid from 20.9% to 10.6%. Additionally, some ketones and aldehydes such as propanone, furanone and acetaldehyde completely disappeared from the bio-oil.

Xiong et al.[75a] performed upgrading of a raw bio-oil using Raney Ni and zeolite-supported Pd and Ru catalysts. The reactions were studied at 423-503 K. Using the Ni catalyst, the oxygen content in the bio-oil was reduced from 31 to 25%. The water content decreased by a factor of 1.5-2. The viscosity also decreased by a factor of 2.5. The authors noted that Ni and Ru were superior to Pd, but that changing the catalyst supports gave insignificant differences. All of this work on in-situ upgrading of bio-oils has therefore shown that formic acid is an efficient hydrogen donor.

Levulinic acid hydrogenation by formic acid to γ-valerolactone. In a patent to the Shell Oil Company[76] in 2007, it was shown that formic acid could be used as a hydrogen donor to convert levulinic acid catalytically into γ-valerolactone (eq. 16), an excellent gasoline additive; Ni/Pt and Re/Pt supported on silica as well as noble-metal-free Cu/Cr oxide were mentioned among the catalysts that could be used for this reaction:



. (16)

Since the publication of this patent, various different catalysts have been tested for this reaction. Ni,[77] Cu,[78] NiCu[79] and Ru[10b, 80] catalysts are of most interest. For example, Upare et al.[79] reported that a Ni(20)Cu(60)-SiO_2 catalyst could selectively convert 99% of levulinic acid into 96% of γ-valerolactone; the remaining 4% of product was angelica-lactone ($C_5H_6O_2$). This catalyst exhibited long-term stability for 200 h without loss in activity at 538 K. The γ-valerolactone obtained could be further hydrogenated to give 2-methyltetrahydrofuran (Figure 8, 2-MTHF, $C_5H_{10}O$).[47a, 81] 2-Methyltetrahydrofuran has already been approved by DOE as an additive to gasoline.

Shell Oil Company researchers[82] have also considered γ-valerolactone as a platform chemical to obtain "valeric biofuels" based on esters of valeric acid ($C_5H_{10}O_2$); this approach can deliver both gasoline and diesel components that are fully compatible with transportation fuel (Figure 8). The basic reaction for this is hydrogenation of γ-valerolactone to valeric (pentanoic) acid over a Pt/ZSM-5 catalyst[82] Further hydrogenation of valeric acid over supported Pd or Pt catalysts gives nonane (C_9H_{20})[83] and this can be used as fuel additive. Serrano-Ruiz et al.[10b] showed that it is possible to convert γ-valerolactone to 5-nonanone ($C_9H_{18}O$) using a doped Pd/Nb_2O_5 catalyst. 5-Nonanone is considered as a diesel or jet fuel component. It can be also further catalytically converted to nonane. Hence, the formic acid formed simultaneously with levulinic acid by the processes described in previous section (Figure 4) can be used to produce γ-valerolactone, which can be further used as an intermediate for fuel additives production.

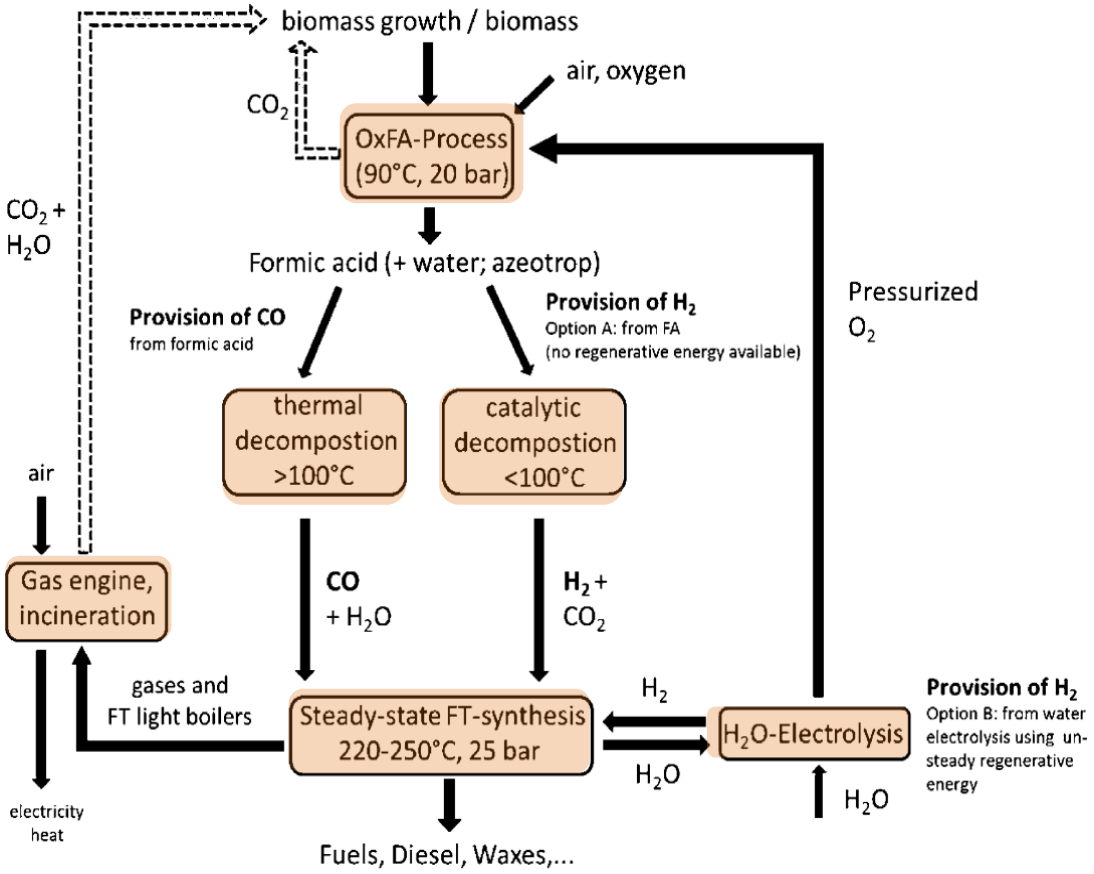


Figure 9. A scheme for the production of hydrocarbon fuels from biomass, water, and renewable electricity in a combination of the OxFA process and Fischer-Tropsch synthesis. Reprinted with permission from ref.[60] Copyright 2016 ACS.

Formic acid conversion to synthesis gas and fuels. The group of Wasserscheid[60] has proposed to combine their OxFA process (allowing them to oxidize different types of biomass into formic acid (CO_2 and water) using oxygen at low temperatures as described above) with two reactors used for the catalytic decomposition of the formic acid, one giving hydrogen and CO_2 (dehydrogenation using metal catalysts) and another giving CO and water (dehydration via thermal decomposition or decomposition using acidic catalysts) as outlined in Figure 9; an additional unit for water electrolysis was added to the system to allow regulation of the gas composition. Using this combination of reactors, a synthesis gas (CO/H_2) feedstock could be created from formic acid and water that was suitable for the Fischer-Tropsch synthesis of hydrocarbons using, for example, a traditional Co/Al_2O_3 catalyst. This approach has an advantage of utilization of low temperatures

for the production of synthesis gas as compared to the production from natural gas, coal or biomass, where the temperatures higher than 900 K are normally needed.[10a, 84] The combined generation of both CO and H_2 in the correct stoichiometry (1:2) for the Fischer-Tropsch reaction leads to the following reaction (eq. 17):

$$3HCOOH \rightarrow CO + H_2O + 2H_2 + 2CO_2. \quad (17)$$

The overall Fischer-Tropsch synthesis reaction of the energy-lean scenario can be represented by (eq. 18):

$$3HCOOH \rightarrow -(CH_2)- + 2H_2O + 2CO_2. \quad (18)$$

As mentioned previously, a suitable catalyst for CO production from formic acid is a ZSM-5 zeolite. These zeolites produce CO with about 100% selectivity at 473 K. Suprunowicz et al.[8] noted that the optimum ZSM-5 catalyst for formic acid decomposition should have the right balance between acidity and hydrophobicity and this can be tuned by changing the Si/Al ratio. A strongly acidic catalyst would be expected to be very active, but would deactivate rapidly due to water adsorption. Hence, a proper tuning of the strength of the catalyst acid sites is needed, but then a question of the catalyst stability may arise.

Because of the advantage that the use of a heterogeneous catalyst allows easy separation and recovery of the catalytic material, they are preferable for the dehydrogenation step even though the activity of a homogeneous catalyst would be significantly higher. For the case of the dehydrogenation of formic acid in the liquid phase, a number of papers have been published giving good results using Pd supported on different carbon supports.[15a, 15b, 85] However, most of the catalysts of these papers were tested only in the conditions of a batch reactor and further studies are needed to prove that they are sufficiently stable under the conditions of a flow reactor.

We have shown that Pd catalysts supported on carbon are very effective for gas-phase dehydrogenation, especially since we have found that they give a significant increase of catalytic activity after doping with K ions;[14a, 14b] at sufficiently low temperatures (<373 K), formic acid condensed in the pores of the catalysts exists in equilibrium with gas phase formic acid. In the presence of K ions a buffer-like solution is formed. The concentration of these K ions determines the concentration of formate ions, which are the reactive intermediates in the formic acid dehydrogenation. We have also shown that these catalysts are stable for at least 22 h and that water vapor does not affect their performance.[14b] Alternatively, as we showed[14c, 86] for the gas-phase reaction, a significant improvement of the catalytic properties could be also reached by N-doping of the carbon support. This leads to the formation of single-atom Pd sites attached to pyridinic-type nitrogen species on the edges of graphene sheets and these show better activity and selectivity than do the sites on the surface of Pd nanoparticles.

The group of Wasserscheid[60] noted that the catalysts used for the Fischer-Tropsch synthesis of hydrocarbons should be stable in high concentrations of steam in a reaction mixture, as biomass conversion involves the formation of large amounts of water. If the catalyst to be used is not stable in a steam environment, the synthesis gas formed by formic acid decomposition has to be cooled prior to the Fischer-Tropsch reactor to condense and separate water. Rytter and Holmen[87] have recently reviewed the effects of steam on Co/Al_2O_3 catalysts. They reported that adding large amounts of water to the reaction mixture results in a loss of activity and a high deactivation rate that is either reversible or irreversible depending on catalyst formulation. Narrow to medium pore size aluminas are particularly sensitive to water addition. Hence, a decrease of the content of steam from the feed stream before the Fischer-Tropsch reactor can be necessary. The strategy proposed as shown in Figure 9 looks interesting, but will require further studies at a pilot scale. The formation of significant amounts of by-product H_2O and CO_2 from formic acid (eq. 18) could be considered as disadvantage.

Formic acid conversion to methanol. Methanol has hydrogen content higher than that of formic acid; it is also cheaper and is well established for use as a fuel. Moreover, it is considered as the platform chemical for a "methanol economy".[88] If formic acid could be cheaply produced from biomass and further converted to methanol at low temperatures, this process could be attractive. Some Ru[89] or Ir[90] homogeneous catalysts based on metal-organic complexes are efficient for the conversion of formic acid to methanol. Thus, Tsurusaki et al.[90d] used an Ir complex containing 5,5′-dimethyl-2,2′-bipyridine in the presence of sulfuric acid and obtained a selectivity of 47% at hydrogen pressure of 4.5 MPa and 323-333 K. The yield of methanol increased linearly by a factor of 3 with an increase of the hydrogen pressure up to 3 MPa. The yields depended also on the concentrations of sulfuric acid and formic acid. The authors noted that formaldehyde could be a reaction intermediate, as proposed earlier by Miller et al.,[90a] but the rate of reduction of this molecule to methanol was much faster than that of its formation from formic acid. Sordakis et al.,[90c] using Ir complexes, reported a methanol yield of 75% when D_2O was used as a solvent at 323 K. They obtained TON values of 1260 using a 9.8 M formic acid solution from five catalytic cycles. Savourey et al.[89] reported the conversion of formic acid to methanol in a 50 % yield when utilizing Ru(II) phosphine complexes under mild conditions.

The basic reactions involved for the conversion of formic acid would be either hydrogenation (eq. 19) or disproportionation (eq. 20):[90d]

$$HCOOH + 2H_2 \rightarrow CH_3OH + H_2O, \qquad (19)$$

$$3HCOOH \rightarrow CH_3OH + H_2O + 2CO_2. \qquad (20)$$

Both reactions are not elementary. The disproportionation reaction could be presented as a combination of reactions of formic acid decomposition giving hydrogen and hydrogenation of the formic acid to formaldehyde and formaldehyde to methanol by this hydrogen (Figure 10).

Savourey et al.[89] have mentioned that methanol can also be obtained from the H_2/CO_2 mixture over their Ru catalyst.

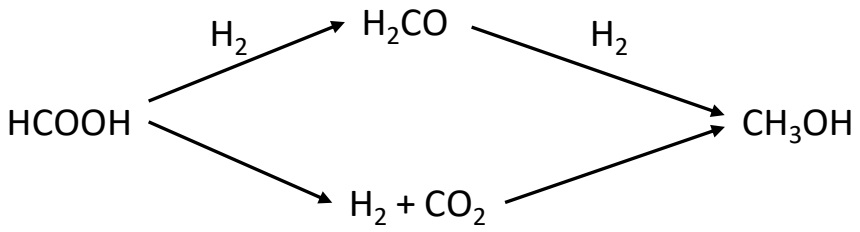


Figure 10. Reaction scheme for the production of methanol from formic acid.

Heterogeneous catalysts have also been used for the synthesis of methanol from formic acid. For example, Liu et al.[91] converted formic acid to methanol using Cu as a catalyst and Zn as a reductant under hydrothermal conditions at 523–598 K. A methanol yield of 32% was achieved at 573 K. The following reaction (eq. 21) was proposed:

$$HCOOH + 2Zn + H_2O = CH_3OH + 2ZnO. \quad (21)$$

To convert the zinc oxide back to metal, these authors suggested using concentrated solar energy.[92] The authors proposed a process which consists of the following steps: rapid decomposition of formic acid to CO_2 and H_2, formation of a large amount of hydrogen and ZnO by the oxidation of Zn by water, and reaction of CO_2 with hydrogen to form methanol over Cu or Cu/ZnO catalysts. It should be noted that direct conversion of a CO_2/H_2 mixture to methanol using Cu/ZnO based catalysts efficiently takes place at high pressures of 5-10 MPa and temperatures of 523-573 K.[16b]

8. Summary and outlook

Therefore, we have shown that a variety of methods for formic acid synthesis have been proposed already by the middle of 19th century. Some of them used biomass-derived products as chemical intermediates. The current technology for formic acid production[3] as well as the recently proposed one[31a] are based on methanol and they have a major disadvantage as methanol has to be obtained by an unsustainable route involving hydrogenation of CO_x gases with hydrogen, which is in turn obtained at very high temperatures from fossil feedstocks such as natural gas or coal. Moreover, CO used as a main intermediate in the current technology is toxic. The direct catalytic oxidation of methane to formic acid can be performed at low temperatures (<373 K), but this reaction does not currently give acceptable yields; moreover, it requires the use of hydrogen peroxide.[37-38, 39]

Hydrolysis or oxidation of biomass cellulose give high yields of formic acid at low temperatures (Figures 5-7). Catalytic oxidation can be done even at lower temperatures than noncatalytic wet oxidation. Moreover, as we showed above this approach allows oxidizing of all types of biomass if corresponding catalysts are used with only side products CO_2 and H_2O. Albert and Wasserscheid[61] noted that formic acid is a chemical product used in high amounts by farmers in the preparation of silage; hence, its synthesis from agricultural biomass wastes at agricultural locations could find broad applications. Formic acid could be also used to produce different fuel additives (Figure 8). However, there is a question: should the biomass-derived products be used for the production of formic acid and fuel additives or they should be used for the production of more value-added products?

Good results have been reported for synthesis of methanol from formic acid by the application of homogeneous catalysts at low temperatures. However, the approach via heterogeneous catalysts could also be further developed. It is important to recognize that methanol

can not only be used as a fuel itself, but that it can be converted to gasoline fuels (Figure 8) via the Methanol to Gasoline (MTG) process commercialized by Mobil in New Zealand in 1985, in which ZSM-5 zeolites are applied as catalysts.[93]

Low temperature, cheap and sustainable production of formic acid from biomass followed by the efficient decomposition of formic acid to give simultaneous hydrogen and CO formation with CO_2 and water as by-products on some catalysts may lead to the development of new technologies for the production of fuels based on synthesis gas obtained from formic acid. The group of Wasserscheid[60] have suggested that instead of operating separate reactors for formic acid decomposition to give CO and H_2O or H_2 and CO_2 (Figure 9), formic acid may be directly fed to a Fischer-Tropsch reactor filled with a Co catalyst. This approach has not yet been studied and may provide interesting results, this extending the range of applicability of formic acid. It is clear, however, that fine-tuning of the particle sizes and nature of the catalyst support properties will be necessary to provide high yields of necessary hydrocarbons.

As another option, one reactor with a catalyst giving dehydrogenation and dehydration of formic acid simultaneously can be used before the Fischer-Tropsch synthesis reactor. There is a major advantage to obtaining synthesis gas from formic acid: low temperature of production (<473 K) as compared to those based on gasification of fossil feedstocks or biomass (>900 K). The catalyst in this reactor should convert formic acid almost completely with selectivity to hydrogen of about 67% to give the optimal ratio of H_2 to CO equal to 2:1. We have observed such a selectivity for an Au/TiO_2 catalyst at about 440 K for the gas-phase decomposition.[94] However, the Au catalysts should be substituted by one containing a much cheaper metal or by even relatively inert material like porous carbon doped with alkali metals,[95] which may work stably in the reaction conditions. Hence, it is to be expected that there will be much more research in this field.

Finally, this review shows that formic acid is a versatile chemical intermediate and that the number of investigations of its reactions is steadily increasing. The developments in the field of formic acid utilization have been stimulated by the development of sustainable methods of formic acid production from biomass and from CO_2 (almost not discussed here), and as a result this may lead to a decrease in price of formic acid and further extension of its applicability.

Acknowledgements

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